UNIVERSITY OF TORONTO

DEPARTMENT OF CHEMICAL ENGINEERING
AND APPLIED CHEMISTRY

PHASE SPLITTING IN COMPLEX HYDROCARBON SYSTEMS

A REPORT PREPARED BY

J. M. SHAW
DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY
UNIVERSITY OF TORONTO
M5S 1A4

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ABSTRACT

Significant fluctuations in the light oil yield obtained from laboratory and pilot scale models of heavy oil upgrading, coal/oil coprocessing and direct coal liquefaction processes, arising from apparently minor perturbations in operating conditions, are frequently attributed to synergism. In this study, some aspects of observed synergistic behavior are explained in terms of relevant liquid-liquid equilibria. Partial phase diagrams for simple and complex hydrocarbon mixtures including model diluent/solvent mixtures, eg., pyrene/naphthalene/tetralin, and bitumen/heavy oil/anthracene oil mixtures are presented. These liquid mixtures are shown to be subject to phase splitting at elevated temperatures. The transition from vapour/liquid to vapour/liquid/liquid occurs at 675 to 700 K. A second transition, to a two phase expanded fluid mixture, was observed at hydrogen/methane over pressures in excess of 15 MPa, in some cases. As the projected or actual operating conditions for hydrogenation processes and the temperature and pressure region over which the mixtures can experience phase splitting overlap, previously reported synergism is related to phase splitting and compounding factors such as catalyst wetting, localized reagent depletion, and model diluent/solvent selection.

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INTRODUCTION

Kinetic studies in heavy oil upgrading, coal/oil coprocessing and direct coal liquefaction are frequently conducted without due consideration for the physical properties of the simple, binary or complex liquids including solvents/diluents under the reaction conditions employed (650-750 K, 10-30 MPa). Consequently, significant fluctuations in light oil yield obtained from laboratory and pilot scale studies, arising from apparently minor perturbations in operating conditions, are frequently attributed to synergistic phenomena (Derbyshire et al., 1982; Chiba et al., 1985; Fouda et al., 1988) when only a small sub set of these data may truly exhibit non additive behaviour. As the reaction conditions associated with the aformentioned processes typically intersect the critical region of one or more of the principal liquid constituents (Reid et al. 1987), complex phase behaviour can be anticipated (Subramaniam and McHugh, 1986; Paulaitis et al., 1983). Phase splitting, for example, is a common phenomenon in the critical and subcritical regions. In addition, hydrogen is a principal reagent in both coal dissolution and oil hydrogenation reactions and hydrogen solubility in liquids is sensitive to composition (Shaw, 1987). Phase splitting and hydrogen solubility can have a direct and significant impact on observed rates for coal dissolution reactions (Shaw and Peters, 1988; Shaw and Peters, 1989), for example, and these phenomena provide a satisfactory explanation for 20 wt% fluctuations in coal conversion arising in pyrene-tetralin mixtures under hydrogen (Shaw et al., 1988) which had previously been attributed to synergism (Derbyshire et al., 1982). While it is not proposed that all "synergistic phenomena" related to these processes can be explained in such a manner, this preliminary success provided a basis for a broader phase analysis, which is the subject of this report.

More specifically, research funded under DSS contract # 23440-8-9084/01-SS concerned the possible role of liquid-liquid equilibria in direct hydrogenation processes for heavy oil, bitumen and coal, eg.; does phase splitting arise in among feed materials(heavy oil, bitumen, coal liquids), or reactor effluent, and if so under what circumstances. The original proposal and working statement are appended. These documents, comprising appendices I & II, provide background information and describe the scope of the research in detail. Aspects of this work have also been published, or will appear in print shortly (Dukhedin et al., 1989a and 1989b)

EXPERIMENTAL

Liquid Degradation

Many of the model compounds and liquids employed are unstable under the operating conditions investigated and the phase data presented should not be construed to be equilibrium data per se. Catalysts are ubiquitous actors in these systems and their effect can only be minimized/directed. Glass liners can reduce the impact of trace pyrrhotite(a well known dehydrogenation catalyst) on reactor walls, but cannot prevent catalytic hydrogenation due to catechol adsorption on stirrer surfaces(Yoshii et al., 1982). Homogeneous isomerization, pyrolysis, and other reactions cannot be neglected at elevated temperatures. The degradation of pyrene (Shaw et al., 1988; Derbyshire et al., 1982) and tetralin (Hooper et al., 1979; Benjamin et al., 1979; McNeil et al., 1983; Penninger and Slatboom, 1976), for example, under a variety of experimental conditions has been reported. At 700 K, the fraction of tetralin degraded to naphthalene and various indenes varies from 0 to nearly 1.00 depending on the phase and the presence or absence of various catalysts. Pyrene conversion to dihydropyrene ranges from 0 to 13^{+}% under similar conditions. The coking tendencies of bitumen and vacuum bottoms are also well known. Compound degradation cannot be ignored or prevented and phase compositions inevitably exhibit a time dependence.

Phase Splitting Experiments

These experiments were carried out in a 2 l PPI autoclave in two modes . The first mode used the entire autoclave which has an inside diameter of 0.095 m and a length of 0.3 m . In the second mode the autoclave was equipped with an insert of i.d 0.05 m and a length of 0.24 m . The second mode was designed so as to reduce the amount of material used during an experiment . The autoclave was placed vertically in a 3000 W muffle furnace and equipped with a magnetically driven stirrer, an internal cooling coil and three heated sample ports. All apparatus components were fabricated from type 316 stainless steel. In the first mode the sample ports were located 0.27, 0.19, and 0.0 m from the top of the autoclave and in the second mode the ports were located 0.22 , 0.12 , 0.00 m from the bottom of the autoclave. All ports were fixed and are identified as ports 1, 2 and 3 respectively. In the first mode of operation the autoclave was stirred at a rate of 15 Hz with a six bladed turbine, diameter located 0.08 m from the base of the autoclave and in the second mode with a two bladed turbine, diameter 0.03 m and located 0.03 m from the base of the insert stirred at a rate of 2 Hz. The

autoclave temperature was maintained within two degrees of a set point using an Athena temperature controller and a manually actuated internal cooling coil.

All model compounds were reagent grade and supplied by Fluka . The anthracene oil was supplied by Allied-Signal and Athabasca bitumen and Venezuela heavy oil vacuum bottoms were supplied by CANMET. Selected properties of these three latter materials are listed in Table 1. The materials and compositions for the experiments are listed in Table 2. Upon loading the autoclave with the reactants, air was removed by flushing and the autoclave was pressurized with hydrogen (or methane) and heated at a rate of 6 K min^{-1} to the first set point. Once the temperature reached the set point, operating parameters were fixed for 0.5 h. Agitation facilitated the acquisition of phase data. However, it proved necessary to cease agitation 0.5 h before sample retrieval so that emulsions, if present, might break (Shaw et al., 1988). Samples were collected in ice cold sample vials and immediately diluted in toluene. Species that did not condense at 273 K were not collected. Following sample retrieval the autoclave was heated to subsequent set points and the procedure was repeated.

Samples were analysed chromatographically. Preliminary screening was performed with a Shizmadzu (GC-6AM) gas chromatograph, equipped with a 0.75 m OV-101 column. The column operating conditions were: column flow, 40 ml min^{-1}; carrier gas, nitrogen; flame ionization detector; temperature program, 433 k for 2 min, 433 to 528 K at 20 K min^{-1} with the final temperature held at 528 K. Mass spectra were obtained using a Hewlett Packard 5987A radiofrequency quadrupole mass spectrometer. Many peaks were not unambiguously identified. Samples (1ul) were injected directly into a 30 m DB-17 column. Column operating conditions were: carrier gas, helium; temperature program, 373 K for three minutes, 373 - 548 K at 20 K min^{-1}. Additional mass spectrum analysis and ASTM standard boiling point data were provided by Shell Canada Ltd.

Liquid Densities

In order to establish optimum locations for the sample ports, approximate density data for the feed materials, under operating conditions, was required. These experiments were conducted with a pressurized glass capillary apparatus placed inside an oven. The internal dimensions of the capillaries were 0.002 m diameter by 0.1 m long. The expansion of the liquid samples with temperature was measured directly and

the density data have a precision of 10 Kg/m^3. A more detailed description of the apparatus is provided elsewhere (Pozzobon et al., 1989).

RESULTS

Material Instability

The instability of compounds under the conditions investigated is exemplified by the chromatograms for the model systems shown in Figures 1 and in Tables 3 and 4. Compounds such as decalin, indene, tetralin are more unstable than naphthalene or pyrene. Tetralin, for example, dehydrogenates to form naphthalene, principally. Indene and benzene derivatives are also produced. The range of degradation products appears to be unaffected by the presence or absence of hydrogen or methane in the mixtures. The extent of degradation and the yield of the various products is affected by the amount of methane or hydrogen present, temperature, and other factors. Although not shown, degradation was not significant at temperatures below 650 K.

Phase Splitting of Model Systems

Results for phase splitting experiments listed in Table 2 are summarized in Figure 2. All systems except naphthalene-indene-H_2 and decalin-indene-H_2 exhibit phase splitting. Illustrative chromatograms for pyrene-tetralin-methane and Athabasca bitumen-Anthracene oil- H_2 comprise Figures 1 and 3 respectively. Relative abundance data for principal peaks of the model systems are listed in Tables 3, 4, 5. A detailed composition analysis for a system 7 sample (Venezeula Heavy Oil-Anthracene Oil-H_2 at 648 K) is shown in Table 6. These data are qualitative in nature. They do not connote absolute compositions and are only used to indicate trends. Many of the peaks are identified tentatively. Phase splitting arises when the spectra of samples extracted simultaneously from the sample ports vary substantially. The Indene-decalin-H_2 system, for example (Table 3), does not exhibit liquid-liquid phase splitting, whereas the pyrene-tetralin-methane (Figures 1, and Tables 4 and 5), Athabasca Bitumen- Anthracene Oil-H_2(Figure 3) and Venezeula Heavy Oil-Anthracene Oil-H_2 (Table 6) systems do exhibit phase splitting. A supercritical transition arises if high molar mass components such as pyrene (Figure 1) appear with substantial abundances in what would normally be a gas phase (Shaw et al., 1988). The Venezuela Heavy Oil-Anthracene-H_2 system also becomes supercritical at 675 K.

Phase compositions, Tables 4-6 are consistent with expectation. Low molar mass species are concentrated in one or more phases and higher molar mass species are concentrated in the other(s). In Table 6, for example, mono and dinuclear aromatics are the principal components in one liquid phase whereas polynuclear aromatics are the principal components in the other. Further qualitative data is provided by Figure 3 where peak 1 is phenanthrene and peak 2 is fluoranthene/pyrene. More detailed evaluation of the differences in phase compositions is hampered by incomplete peak identification.

Initial gas phase composition and pressure also contribute to phase splitting. For the model system tetralin-pyrene phase splitting arises at ~693 K in the absence of an initial gas cover(degradation products including hydrogen are produced in situ), whereas at initial methane pressures of 5MPa and 12 MPa phase splitting occurs at temperatures in excess of 650 and 670 K respectively. At initial hydrogen pressures of 3.5 and 5.5 MPa phase splitting arises at temperatures in excess of 675 K (Shaw et al., 1988). Thus systems involving methane, a typical constituent of recycle gas in pilot scale studies, would appear to be more susceptible to phase splitting than those including hydrogen as the principal gas phase constituent. Consequently, phase splitting involving coal liquid-heavy oil mixtures and model solvents/diluents cannot be precluded a priori at temperatures greater than 650 K.

Phase Splitting of Complex Liquids

None of the feed materials(Athabasca bitumen, Venezuela vacuum bottoms, anthracene oil) exhibit phase splitting at temperatures less than or equal to 698 K. As described above, 50 wt % mixtures of anthracene oil and bitumen or Venezuela vacuum bottoms exhibit phase splitting at temperatures above 673 K and 645 K respectively. The upper and lower composition bounds for phase splitting in these systems are currently being determined. Reactor effluent from CANMET bench scale unit trials BB127270587 1&2, and BA125220587-1 & BA114250287-2, which included approximately 25 wt% coal derived liquid(the feed comprised 70 wt% bitumen or vacuum bottoms and 30 wt % coal. The coal conversion was approximately 85 %), do not appear to exhibit phase splitting at or below 698 K under 5 MPa hydrogen pressure. However, the lower composition bound is likely to be in the 30+ wt% range. The reactor effluent samples were too small to permit further phase analysis with these materials.

Liquid Densities

The densities of Athabasca bitumen and Venezuela blend 24 vacuum bottoms decrease rapidly with temperature- figures 4a and 5a. The densities at room temperature exceed the densities at 350 °C by greater than 20 %. The impact of dissolved hydrogen on liquid density appears to be variable. The density of Venezeula blend 24 vacuum bottoms is vertually the same whether or not hydrogen is present [figures 5a and 5b], while the density of Athabasca bitumen is substantially greater in the presence of hydrogen [figures 4a and 4b].

DISCUSSION

Phase Splitting and Synergism

Fouda et al., 1988 report the effect of coal concentration on coprocessing performance and note a synergistic increase in distillate yield at low coal concentrations, which may be attributed to catalytic phenomenon. Their data also show a sharp decrease in distillate yield from pitch (+780 K fraction of the heavy oil) at approximately 30 wt% coal. Pitch conversion at 725 K drops from 70^{+} % to as little as 50 % as coal content rises from 30 to 40 wt %. Coal conversion remains unaffected at 85 wt%. Consequently, the distillate produced shifts from 33 to 50 wt % coal derived species. Our results show that phase splitting occurs at less than 50 wt % coal liquid (heavy oil-coal liquid samples extracted from the autoclave had final boiling points less than 790 K) and the sharp reduction in pitch conversion may be attributed to phase splitting in a manner analogous to that described previously for coal conversion (Shaw et al., 1988) eg., poor liquid-liquid mass transfer leading to potential hydrogen starvation in the dispersed liquid phase; the concentration of large multifunctional molecules in a single phase with a low hydrogen solubility which promotes polymerization "coking" reactions to occur. It is also worth noting that coal based catalysts, such as mineral matter and catechols, and the pitch may not be in the same phase once phase splitting occurs.

Synergistic coal conversion fluctuations realized with the indene-decalin solvent system (Chiba et al., 1985) are not readily attributed to phase splitting as the solvent components, though unstable, do not appear to exhibit phase splitting. The potential role of phase phenomena in the indene-decalin-coal liquid system is currently under investigation.

Prediction of Phase Splitting

-Introduction

Phase splitting, the tendency for components comprising a single liquid phase to separate into two liquid phases with differing composition, is related to the thermodynamic stability of a mixture (Modell and Reid, 1983). The thermodynamic criteria for phase splitting, many of which are equivalent, involve derivatives of chemical potential, entropy, enthalpy, and free energy. The number and complexity of the criteria is related to the number of chemical species present. Chemical species can be whole molecules, or molecular segments if a group contribution approach is adopted. The criterion most easily accessed experimentally is the one involving excess Gibbs free energy, where phase splitting arises in a three component mixture, for example, if

$$\delta^2 g^E/\delta x_2{}^2 + RT\,[a^2/x_1 + 1/x_2 + (1-a)^2/x_3] < 0 \qquad (1)$$

$a = (\delta x_1/\delta x_2)_{\mu_1}$ and $\mu 1$ is chemical potential

There is no unique form for the excess Gibbs free energy function and several models have been proposed for multicomponent mixtures: Margules (4 models), Wilson, NRTL, UNIQUAC/UNIFAC, MOSCED (limited to predictions at 298 K). Although these models vary in complexity and generality, all of them contain parameters which must be evaluated from binary liquid-liquid and liquid-vapour equilibrium data. Optimum parameter sets, generated from such data, are not unique. More over model predictions for ternary or higher liquid-liquid equilibria are sensitive to the values of these parameters so some multicomponent liquid-liquid equilibrium data is needed to ensure reliable estimates. Consequently, phase splitting cannot yet be predicted a priori. The models can only be used to interpolate and extrapolate existing data sets within well circumscribed bounds. However, it is worth noting that multicomponent vapour-liquid equilibria are well represented by the above models.

-Model Restrictions

1. The Wilson equation can only be used to predict free energies of mixing and activities within the single phase region, as it does not even qualitatively predict phase splitting.
2. The UNIQUAC/UNIFAC approach does not as yet include parameters for hydrogen, methane, nitrogen or their respective subgroups (Prausnitz, private communication, May 1989) and is not applicable to the mixtures considered. Two parameters must be evaluated from multicomponent data for each binary pair.

3. Three parameters must be evaluated from multicomponent data for each binary pair when the NRTL equation is employed. These parameters are temperature sensitive and much data is required.
4. The simplest form of the Margules equation includes a single parameter for each binary pair. These parameters are also temperature sensitive.

-Model Selection

The simplest form of the Margules equation

$$G/RT = 1/2\Sigma_i\Sigma_j (A_{ij} x_i x_j) + \Sigma x_i \ln x_i \qquad \text{where} \quad Aii = 0 \quad Aij = Aji \qquad (2)$$

was selected and the number of parameters was reduced by taking advantage of the fact that the hydrogen, nitrogen, or methane mole fractions in the two liquid phases is approximately equal, and that the interaction parameters between these species and individual liquid constituents are also similar. Thus for a ternary mixture there are only 2 parameters, at any given temperature. For the hydrogen/tetralin/pyrene ternary $A_{12} = A_{13} = 0.95$ and $A_{23} = 2.3$ at 698 K and the phase splitting data are well represented- figure 6.

-The Roles of Temperature and Pressure

Liquid mixtures which exhibit phase splitting typically have a lower or upper consolate temperature. That is to say that phase splitting arises above or below a fixed temperature. Mixtures exhibiting both lower and upper consolate points are extremely rare. As the liquid mixtures in question all exhibit a lower consolate point, it is unlikely that the two phase zone can be exited simply by raising the temperature. The role of pressure is confounded by the link between pressure and composition. However, in both cases the trends are the same. Single liquid phases are preferred at elevated pressures.

-Role of Gas Phase Constituents

Each gas component such as hydrogen, nitrogen, or methane has a different interaction parameter with the liquid, all of which vary with temperature. Consequently, the pressure temperature composition region where there are 3 or more roots to equation 2, ie. the region where phase splitting occurs, is sensitive to gas phase composition- figure 7. Such shifts with respect to gas phase composition are readily predicted as long as the respective binary coefficients are known.

-Complex Liquid Mixtures

The theoretical treatment of complex liquid mixtures is beyond the scope of this work. However, two approaches are possible:

1. Combine the generality of the UNIFAC/UNIQUAC model for the oil constituents with activities for gas constituents obtained through experiment or by regressing data available in the literature. In order for such an approach to be successful, liquids would require extensive characterization by functionality so that group contributions could be computed. Some functional groups are listed in Table 7. At a minimum the most prevalent groups would have to be quantified. The temperature dependence of the associated parameters would have to be ignored.

2. An alternative approach would be to divide heavy oils and coal liquids into three or more general classes: aromatics 1: up to three rings

aromatics 2: 4 or more rings

aliphatics 1: branched

aliphatics 2: unbranched

and represent each complex mixture as a combination of the appropriate groups. Binary interaction parameters would be established from model compound data which represent each group.

The second approach is likely to provide specialized but usable results within a shorter period of time and be more cost effective in the short run. In the longer term, the first approach is likely to be preferred as the results would link up with predictions of vapour-liquid equilibria and other properties. All data collected would of course be relevant to both approaches.

CONCLUSIONS

Liquid behaviour is poorly understood on a molecular level. Our theoretical tools are correspondingly primitive and our ability to predict phase behaviour is restricted. In addition the degree of molecular difference need not be great for phase splitting to occur, and minor components can have a significant impact on the region over which phase splitting occurs. The investigation of liquid-liquid equilibria at elevated temperature and pressure remains primarily a matter for experimental rather than theoretical consideration.

Significant fluctuations in distillate yield obtained from laboratory and pilot scale coal/oil coprocessing and direct coal liquefaction processes, arising from apparently minor perturbations in operating conditions can be explained, in part, by phase splitting. Relevant model and complex liquid mixtures are shown to be subject to phase splitting at elevated temperatures. The transition from vapour-liquid to vapour-liquid-liquid can occur at temperatures as low as 650 K. As the projected or actual operating conditions for hydrogenation processes and the temperature and pressure region over which the mixtures can experience phase splitting overlap, previously reported synergistic behaviour is related to consequential phenomena including: hydrogen depletion in the dispersed liquid phase, polymerization reactions and the distribution of catalyst among the phases. In the case of coal/oil coprocessing, phase splitting would only appear to arise at coal concentrations in excess of 30 wt%, which is outside of the range normally encountered. However, further investigation is warranted.

RECOMMENDATIONS

1. In order to provide more than binary answers to the question does phase splitting occur in complex liquids, more must be learned about appropriate molecular interactions. Experimental determination of characteristic interaction parameters (between alaphatic and aromatic hydrocarbons etc.) at elevated temperatures is essential to this understanding. It is only with such data that diluent/solvent composition can be optimized.
2. The solubility of product liquids in feed materials, while of a more applied nature, is essential in scale-up as such data delimit the extent of axial mixing which can be tolerated in a scaled up reactor sequence.

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TABLE 1: Physical Properties and Compositions of Oils (wt %)

		Anthracene Oil	Athabasca Bitumen	Venezuela (blend 24)
Specific gravity		(15.5°C) 1.092	(24°C) 1.046	(21°C) 1.026
water, %		0.2	-	-
xylene insoluble, %		0.08	-	-
pentane insoluble, %		-	38.4	21.4
Distillation, % to	498 K	0.0	-	-
	543 K	7.9	-	-
	588 K	43.7	-	-
	628 K	80.5	-	-
	+628 K	19.0	-	-
	+798 K	-	99.3	95.1
Elemental Analysis	C		84.3	84.3
	H		10.9	9.6
	N		0.8	0.7
	O		0.3	0.7
	S		3.5	6.0
Aromatic Carbon, %			35.4	30.0
Mean Molar Mass			983	848

TABLE 2: Experimental Systems

System	Anthracene oil	Mass (g)	WT %
1	Decalin	175	60
	Naphthalene	120	40
2	Decalin	200	63
	Naphthalene	120	37
3	Decalin	150	50
	Indene	150	50
4	Decalin	193	35
	Indene	101	65
5	Decalin	75	25
	Indene	225	75
6	Naphthalene	65	28
	Decalin	160	69
	Pyrene	1	3
7	Anthracene oil	175	49
	Venezuela	175	49
	Pyrene	6	2
8	Anthracene oil	400	48.8
	Venezuela	400	48.8
	Pyrene	10	1.2
	Naphthalene	10	1.2
9	Anthracene oil	150	49
	Venezuela	150	49
	Pyrene	6	2
10	Anthracene oil	150	50
	Athabasca	150	50
11	Pyrene	45	25
	Tetralin	135	75
12	Pyrene	45	25
	Tetralin	135	75

Systems 1-10 had an initial hydrogen pressure of 5 MPa
System 11 had an initial methane pressure of 5 MPa
System 12 had an initial methane pressure of 12 MPa

TABLE 3: System #4 at 673 K

Number	Compound	Relative Abundance	
		A	B
1	Unidentified	15	9
2	C9H8	16	14.8
3	Decalin	8.3	5.8
4	1H-Indene 2,3 dihydro 1 methyl	8.3	5.2
5	C10H8	3.4	3.2
6	Naphthalene	37	38

TABLE 4: System #12 at 688 K

Number	Compound	Relative Abundance		
		A	B	C
1	C9H10	14.4	9.3	6.0
2	1H-Indene 2,3 dihydro 1 methyl	7.2	4.1	4.0
3	Tetrahydro naphthalene	2.4	39.8	36
4	Naphthalene	7.5	30.6	27
5	Pyrene	18.5	16.2	27.4

TABLE 5: System #11at 688 K

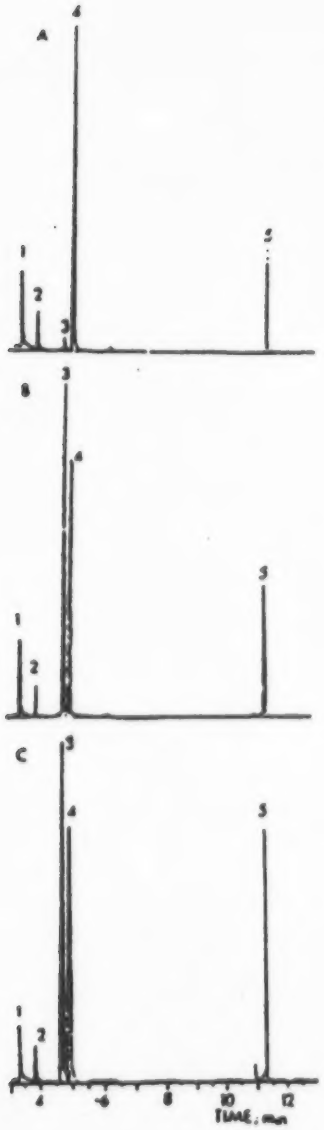
Number	Compound	Relative Abundance		
		A	B	C
1	C9H10	15	9	16
2	1H-Indene 2,3 dihydro 1 methyl	4	20	17
3	Tetrahydro naphthalene	0	22	8
4	Naphthalane	55	34	45
5	Pyrene	27	15	14

TABLE 6: System #7 at 648 K

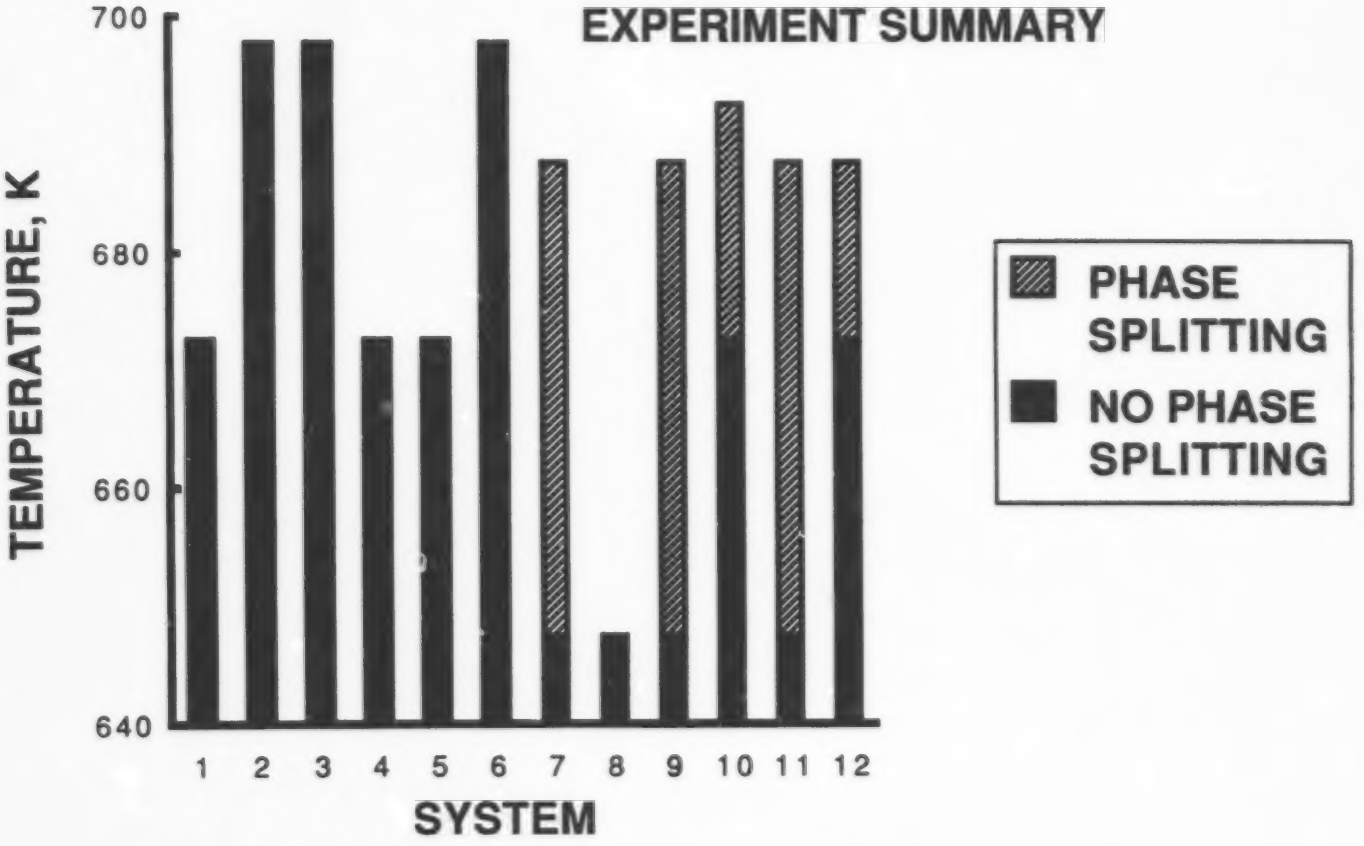
Number	Compound	Relative Abundance	
		A	B
1	Ethyl benzene	4.2	4.6
2	1,3-Dimethyl benzene	7.0	5
3	1,2-Dimethyl benzene	3.6	2
4	Naphthalene	19.7	7
5	1-H-Indene 1-ethylidene	16.3	
6	1,4-Methano naphthalene,1,4-dihydro	3.8	1
7	1,4-Methano naphthalene-9-one tetrahydro	5	4
8	Dibenzofuran	3	4.5
9	9-H-Fluorene	6.3	14.7
10	Phenanthrene	0	16.7
11	Benzene,1,1-(1,2-Ethyldiyl)	19.7	17
12	1-H-Indene, 1-(Phenylmethylene)	3.8	4.5
13	Fluoranthene	7.5	14

TABLE 7 **UNIFAC Group Specifications**

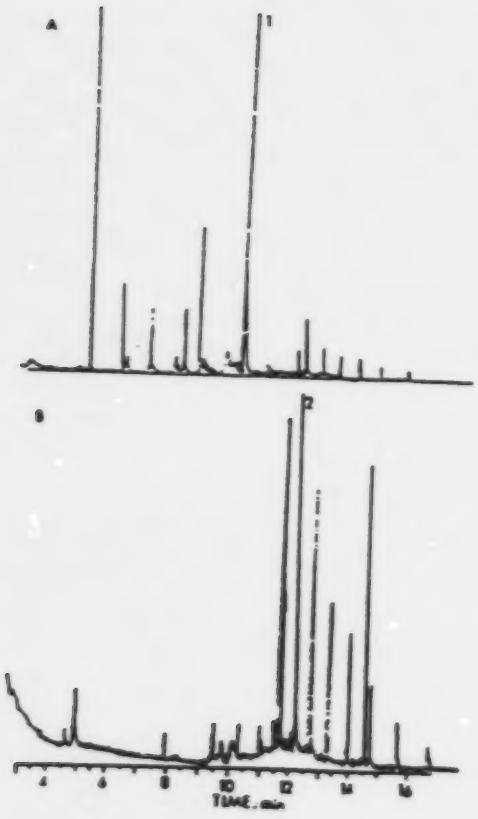
CH_3	CF_3	CH_3CO	CH_3N	$ACNO_2$
CH_2	CF_2	CH_2CO	CH_2N	
CH	CF			CS_2
	COO			
C		CHO	$ACNH_2$	
$CH_2{=}CH$				CH_3SH
$CH{=}CH$				CH_2SH
$CH_2{=}C$	SiH_3		C_5H_5N	
$CH{=}C$	SiH_2	CH_3COO	C_5H_4N	Furfural
$C{=}C$	SiH	CH_2COO	C_5H_3N	
ACH	Si		CH_3CN	$(CH_2OH)_2$
AC	SiH_2O		CH_2CN	
$ACCH_3$	SiHO	HCOO		I
$ACCH_2$	SiO		COOH	
ACCH			HCOOH	
OH	*tert*-N			BR
		CH_3O	CH_2Cl	
		CH_2O	CHCl	
		$CH{-}O$	CCl	CH-trip-C
CH_3OH	Amide	FCH_2O	CH_2Cl_2	C-trip-C
		CH_3NH_2	$CHCl_2$	
H_2O		CH_2NH_2	CCl_2	Me_2SO
	$CON(Me)_2$	$CHNH_2$	$CHCl_3$	
ACOH	$CONMeCH_2$		CCl_3	Acry
	$CON(CH_2)_2$	CH_3NH		
		CH_2NH	CCl_4	$Cl(C{=}C)$
		CHNH		
			ACCl	
			CH_3NO_2	
			CH_2NO_2	
			$CHNO_2$	



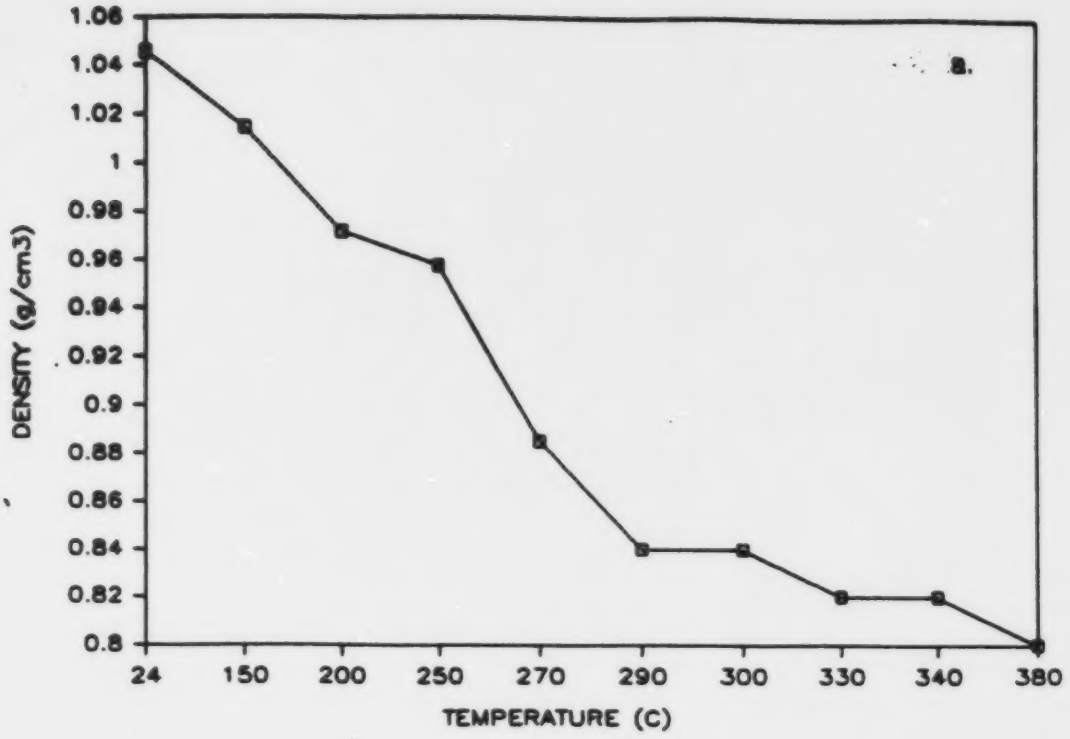
1. System 12 at 688 K: chromatograms A,B and C refer to the gas phase and the two liquid phases respectively



2. Phase Splitting Experiment Summary for Model Systems



3. System 10 at 688 K: chromatograms A and B refer to the two liquid phases respectively



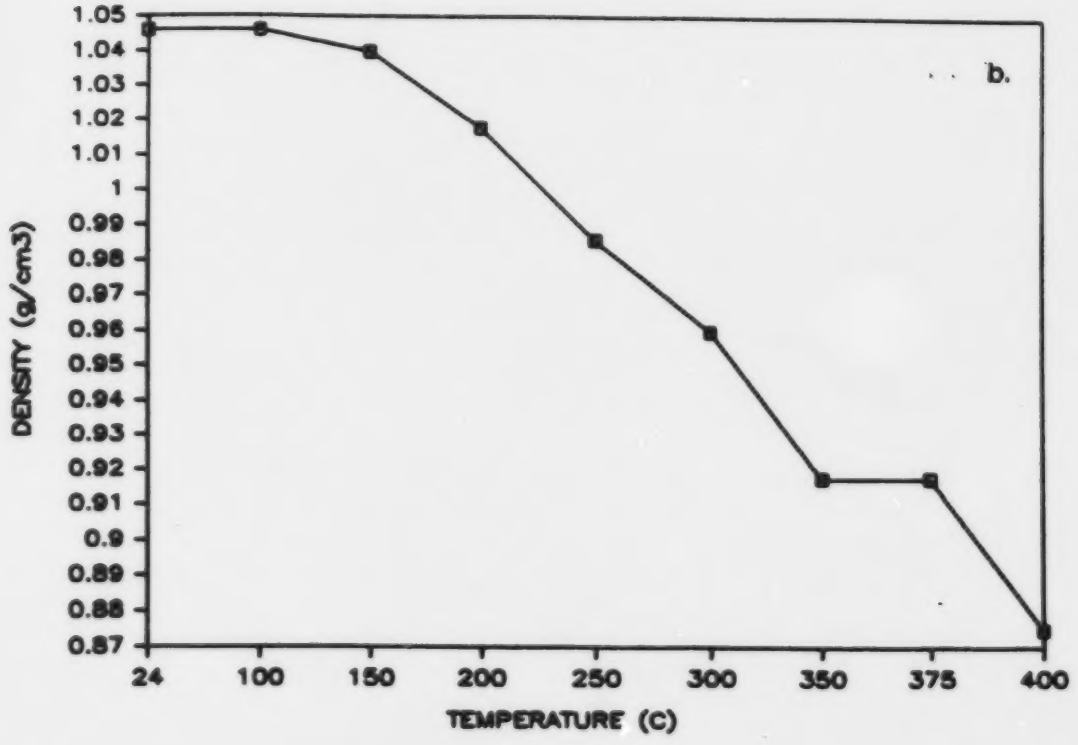
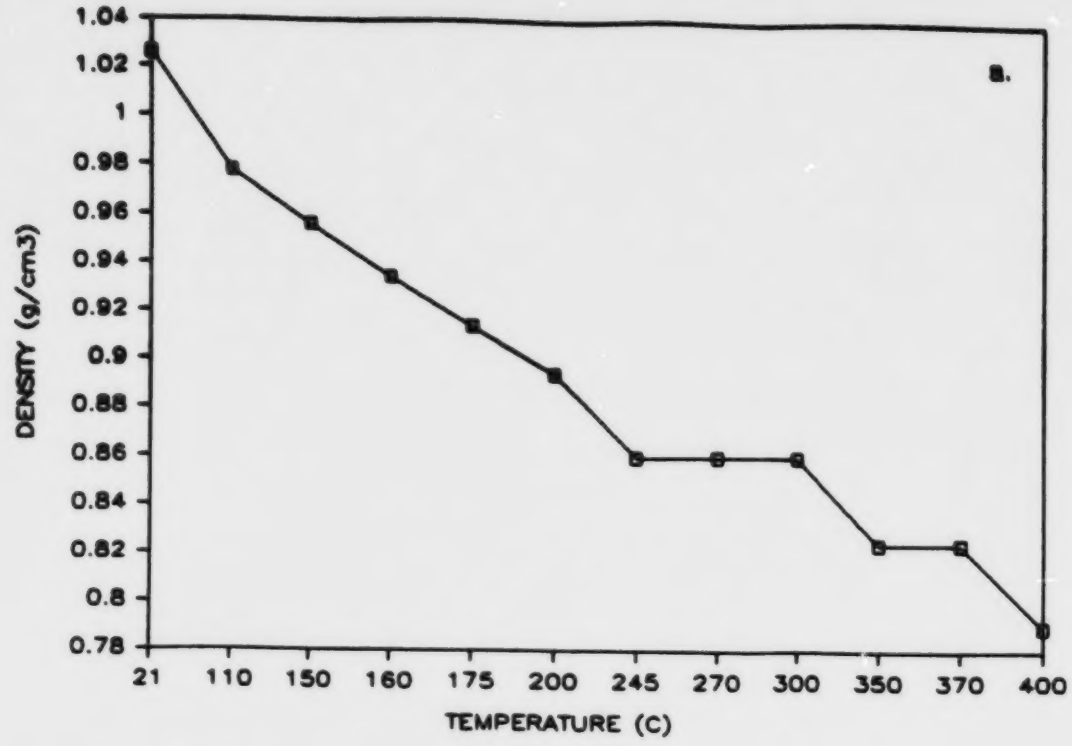


FIG 4a. ATHABASCA BITUMEN

FIG 4b. ATHABASCA BITUMEN WITH HYDROGEN (800 psi)



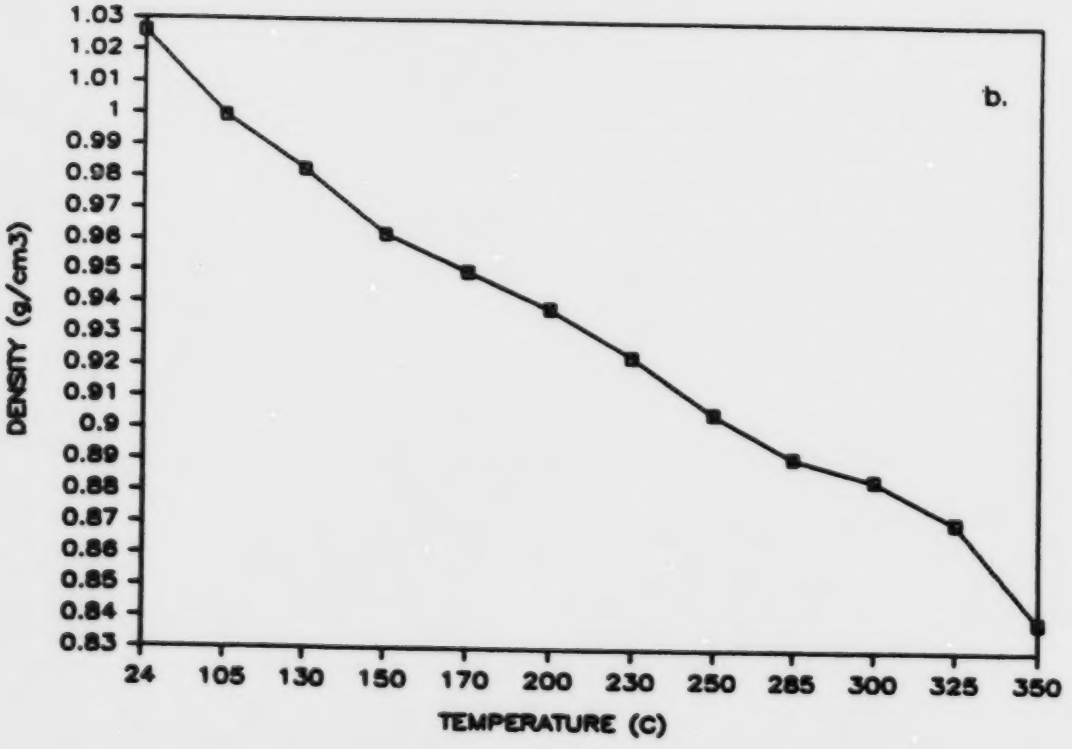
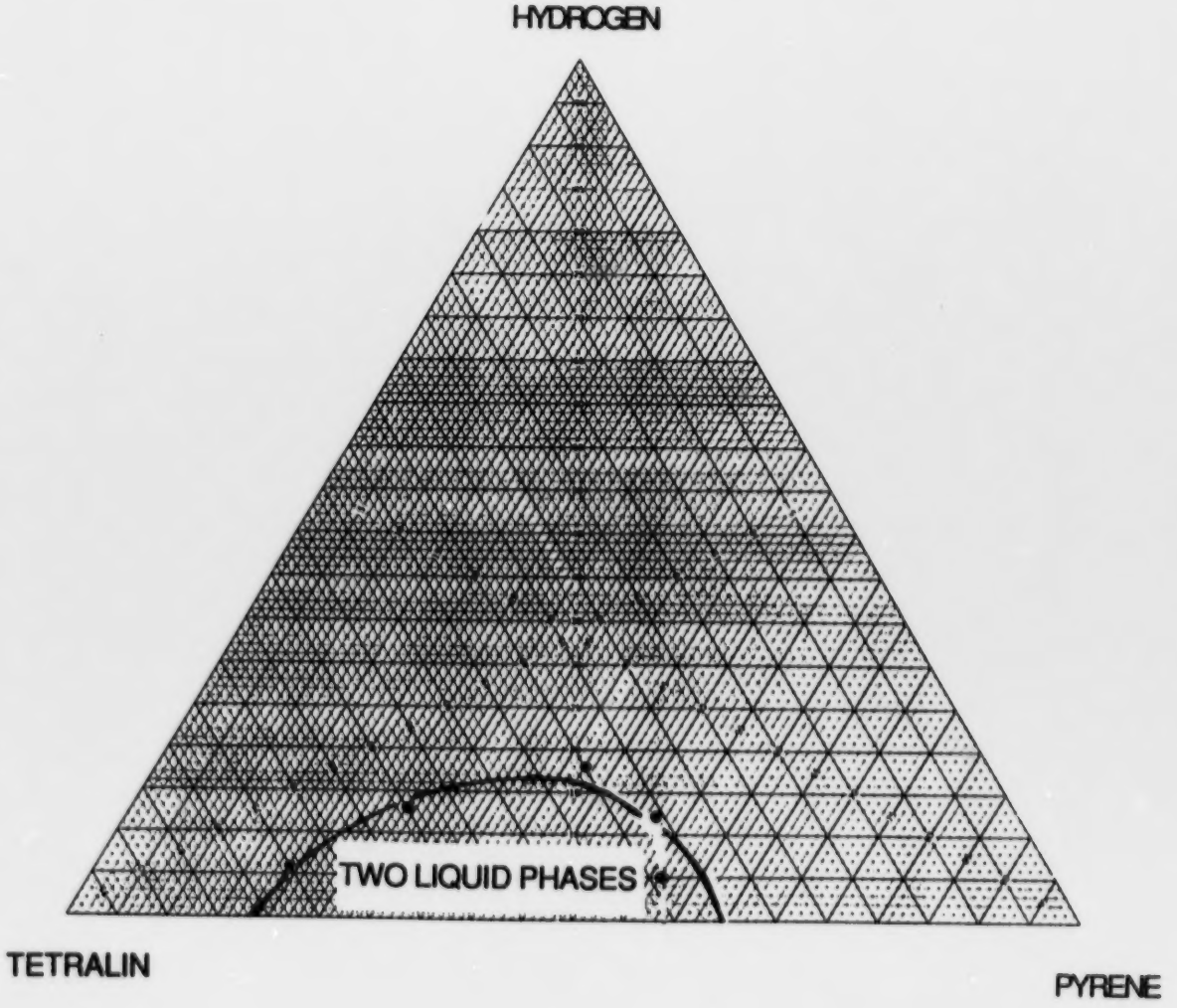
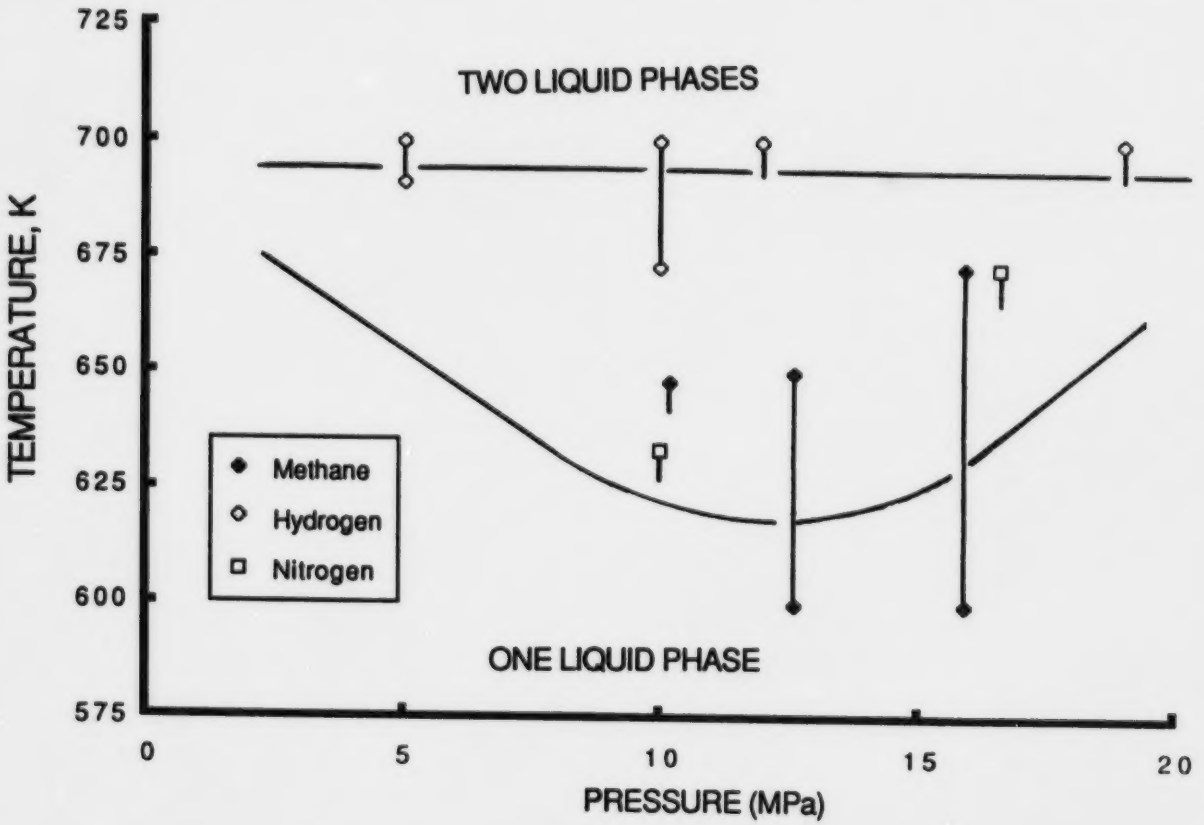


FIG 5a. VENEZUELA BLEND 24 (VACUUM BOTTOMS)

FIG 5b. VENEZUELA BLEND 24 (VACUUM BOTTOMS) WITH HYDROGEN (700 psi)



6. Partial Ternary Diagram for the Pyrene Tetralin Hydrogen system at 698 K



7. The Impact of Gas Phase Composition and Pressure on Phase Splitting in the Tetralin-Pyrene System

APPENDICES

JOHN M. SHAW

Project Title: The Role of Liquid-Liquid Equilibria in Direct Hydrogenation Processes for Bitumen and Coal

Summary:

As reserves of conventional mineral oils dwindle our dependence on bitumen and coal reserves as sources for liquid transportation fuels and petrochemical feedstocks will continue to grow. Currently 8% of the oil consumed in Canada is derived from bitumen. The conversion of coal to transportation fuels is not yet economically viable. However, technology must be developed to facilitate the transition from mineral oil to bitumen to coal, as it is only in this manner that serious economic dislocation can be averted prior to the advent of large scale renewable energy and chemical resources.

Direct hydrogenation is one of the competing technologies that can be used to up-grade both coal and bitumen with relatively high yields of salable liquid products. In these processes, the material to be up-graded is first combined with hydrogen gas and a fraction of the oil product. This mixture is then reacted at elevated temperatures and pressures. Bitumen and coal are processed in a similar manner and some process routes, such as CANMET, can be adapted to process either bitumen or coal.

The reaction environment and kinetic schemes associated with direct hydrogenation processes are complex. In addition to vapour and solid, two liquid phases may also co-exist in these processes. As the transfer of hydrogen between liquid phases is slow, the liquid phase which is not in direct contact with the hydrogen gas may become deficient in hydrogen as hydrogenation reactions progress. In the absence of hydrogen, solid products with a low commerical value tend to be formed. Substantial improvements in these processes may be realized, if the liquid fraction reporting to the second liquid phase is minimized. We have previously shown that the model solvent/diluent system (pyrene-tetralin) exhibits phase splitting at temperatures greater than 690K (Shaw et al., 1988). This phenomenon may also arise in the CANMET Co-Processing reaction sequence.

We propose to determine the processing conditions under which two liquid phases are present in the CANMET Process. A phase equilibrium apparatus, funded by an NSERC grant, and analytical support services are available for this purpose. The expected results will play a role in optimizing existing direct hydrogenation processes for bitumen and coal and may lead to the development of improved processing concepts.

Background Information:

As reserves of conventional mineral oils dwindle our dependence on bitumen and coal reserves as sources for liquid transportation fuels and petrochemical feedstocks will continue to grow. Currently, 8% of the oil consumed in Canada is derived form bitumen. The conversion of coal to transportation fuels is not yet economically viable. However, technology

must be developed to facilitate the transition from mineral oil to bitumen to coal, as it is only in this manner that serious economic dislocation can be averted prior to the advent of large scale renewable energy and chemical resources.

Direct hydrogenation is one of the competing technologies that can be used to up-grade both coal and bitumen with relatively high yields of salable liquid products. In these processes, the material to be up-graded is first combined with hydrogen and a fraction of the oil product. This mixture is then fed to a reactor, where the hydrogenation/cracking reactions are conducted at elevated temperatures and pressures. Bitumen and coal are processed in a similar manner and some process routes (H-COAL/H-OIL, CANMET KOHLE-OEL) can be adapted to process either bitumen or coal. Reactor designs for the direct hydrogenation of coal and bitumen, including such processes as H-COAL, KOHLE-OEL, and CANMET are described in detail elsewhere (Shaw, 1985; Menzes et al., 1981).

The proposed project is an integral part of a broader research programme aimed at determining the number of phases present in complex reaction systems, and the constraints thereby imposed on reaction kinetics and possible contacting schemes. Particular emphasis has been placed on systems involving two liquid phases. Most recently this work has concerned reactor design for direct coal-hydrogenation processes. A series of experiments provided qualitative support for the existence of two liquid phases in coal hydrogenation processes (Shaw and Peters, 1987a). This led to the development of a general mathematical model for coal dissolution reactions (Shaw and Peters, 1987b) and a proposal for an improved reactor design for direct coal-hydrogenation processes (Shaw and Peters, 1986). The hydrodynamics associated with gas-liquid-liquid systems are currently under investigation in a related project (Hatzikiriakis et al., 1988).

Phase splitting of organic liquid mixtures as a consequence of critical phenomena and/or chemical dissimilarity is well known and is exploited in a variety of contexts to affect separations (Subraminiam and McHugh, 1986). However, possible dileterious effects associated with phase splitting in direct hydrogenation processes for bitumen and coal have not previously heen addressed in detail. These effects include the impact of phase splitting on the availability of hydrogen in the liquid phases. Hydrogen solubility is a strong function of liquid composiiton (Shaw, 1987), and the rate of hydrogen transfer between liquid phases is limited. As hydrogen is a key reagent in these processes, hydrogen depletion can lead to excessive coke formation and can reduce the space-time yield of salable liquid products. A preliminary series of phase splitting experiments performed with the tetralin-pyrene solvent system (Shaw et al., 1988) provided a basis for explaining fluctuations in coal conversion and liquid product quality with soluent compositon, previously attributed to synergism (Derbyshire et al., 1982; Chiba et al., 1985).

The high boiling fraction of bitumen (to ≥400°C) typically fed to direct hydrogenation processes such as CANMET comprises a complex mixture of straight chain aliphatic and polynuclear aromatic compounds. In addition, the hydrogenated and cracked reaction products are structurally and functionally different from the feed material (Selucky et al., 1978; Menzes

et al., 1981). Thus, bitumen may possess two liquid phases on entry to a reactor, or a second liquid phase may arise within a reactor, depending on the degree of axial mixing, and the rate at which various species are hydrogenated/cracked.

Thermally fractionated samples of coal liquids, bitumen and hydrogenated bitumen will be combined in an effort to simulate bulk liquid compositions in existing and proposed reactors and to define minimum and maximum loadings of the higher boiling fractions which prevent a second liquid phase from forming under the anticipated range of operating conditions.

Objectives:

The principal objective of this research is to elucidate the link between the existence of two liquid phases and the performance of direct hydrogenation reactors.

More specifically we plan to:

1. Determine the processing conditions under which two liquid phases are present in the CANMET Process.
2. Propose improvements for the design or operation of the CANMET hydrogenation reactor.

Research Plan and Methodology:

The phase equilibrium apparatus, and analytical support facilities including gas chromatography and standard chemical and thermal fractionation techniques are already in place. Much of this equiopment was purchased with funds obtained from NSERC. Additional analytical services are available within the department on a cost recovery basis. As elements of this apparatus were employed in studies cited above, few equipment related problems are anticipated.

All phase equilibrium experiments will be conducted in a 2 litre PPI autoclave equipped with magnetically driven stirrer and heated sample ports. The autoclave will be relined so that liquid samples of ~200 to 300 grams can be processed. The autoclave can be heated rapidly to temperatures in excess of 400°C and temperature is controlled automatically with an external heating mantle to within 2°C of a set point. The reactor is located in a fumehood and can be sampled safely. The sampling devices comprise fine steel tubes and manually operated metering valves. The sample ports are located at various elevations within the autoclave, and liquid passes through the tubing and valves into chilled receiving vessels. The receiving vessels are partially filled with diluent and any vapour escaping from the receiving vessels flows into an adjacent exhaust duct.

Thermal degradation of samples during heating and equilibration is inevitable and the data obtained will be semi-quantitative. The sample ports may also become plugged under certain operating conditions. The extent of degradation can be determined by standard thermal or chemical fractionating

techniques, and this problem can be minimized by: reducing the exposure time at elevated temperatures -- direct injection of liquid into a preheated autoclave can be performed with this apparatus, and by controlling the nature of the degradation through hydrogen addition.

Assessment of Data:

The accuracy and precision of composition data will depend primarily on the quality of the samples obtained from the apparatus. Little uncertainty will be introduced through the proposed instumental analytical techniques (GC and HPLC), and the thermal and chemical separation techniques are only intended to provide semi-quantitative results. Characteristic chromatographic spectra have been obtained for anthracene oil and other complex liquids with existing equipment. We plan to identify bitumen in a similar manner. If this approach fails, liquids will be doped with low concentrations of two characteristic compounds, (eg.) naphthalene and pyrene, prior to phase equilibrium experiments, and differences in phase compositions will be identified by the ratios of the characteristic peaks.

Significance:

The reaction environment and kinetic schemes associated with the direct hydrogenation of bitumen and coal liquids are complex. In addition to vapour and solid, preliminary experiments indicate that two liquid phases may also co-exist in these processes under certain operating conditions. As interfacial mass transfer between condensed phases is slow, the liquid phase which is not in direct contact with the gas phase may become hydrogen deficient as hydrogenation reactions progress, thus reducing the rate of hydrogenation of this material and or promoting retrogressive coking/polymerization reactions. Substantial improvements in the ultimate yield or spacetime yield of salable liquid products from bitumen and coal may accrue, if the liquid fraction reporting to the second liquid phase is minimized. The results of this research will play a role in optimizing a broad range of direct hydrogenation processes for bitumen and coal.

Budget:

The various costs associated with the proposed ten week experimental programme are tabulated below. The total proposed cost for the project is $24,962.50.

Personnel			
Principal Researcher	5 days × $200.00 per day =	1000.00	
Post Doctoral Fellow	50 days × 130.00 per day =	6500.00	
Visiting Chinese Scholar	50 days × 65.00 per day =	3250.00	
Research Assistant	50 days × 50.00 per day =	2500.00	
Total Salaries			$13,250.00
Overhead Charges: (65% of 13,250)			$8,612.50
Supplies and Materials			800.00
Travel* meetings with CANMET officials			700.00
Report Preparation			400.00
Technical Services Machine shop and analytical support			1,200.00
TOTAL			$24,962.50

*(including 2% overhead)

Personnel:

The research team comprises Professor J.M. Shaw, Dr. R.P. Gaikwad, Mr. S. Yushun and a research assistant. The principal investigator and Dr. Gaikwad have extensive experience in this research area. Their resumes are attached for you perusal.

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Subramaniam, B., M.A. McHugh; Ind. Eng. Chem. Process Des. Dev., Vol. 25, pp. 1-12 (1986).

Shaw, J.M., R.P. Gaikwad and D.A. Stowe, "Phase Splitting of Pyrene-Tetralin Mixtures under Coal Liquefaction Conditions", in press, Fuel (1988).

Hatzikiriakos, S.G., R.P Gaikwad and J.M. Shaw, "Characterization of Gas-Liquid-Liquid Tubular Reactors", to be presented at the A.I.Ch.E. National Meeting, New Orleans, March 8, 1988.

APPENDIX II: Working Statement

Phase I: Start-up

Tasks

1. The evaluation of liquid densities at low and high hydrogen pressures. 10 experiments are planned:

   - 2 feed materials X 2 hydrogen pressures
   - 1 standard performed with tetralin
   - 2 product materials (low + high severity) X 2 hydrogen pressures
   - 1 duplicate

2. Apparatus Modification
   - installation of new sample ports/supports
   - manufacture of glass/steel reactor liners to reduce the reactor size to 0.5 litres, and facilitate handling of the materials
3. Development of GC analysis technique(s) for preliminary screening of samples.
4. Leak testing of the apparatus, finalization of procedures and operating conditions, preliminary experiments.

Phase II: Liquid-Liquid Equilibria in the Feed Materials

Liquid-liquid equilibria arising in the bitumen and heavy oil samples supplied by CANMET will be evaluated over the temperature range 350 - 425 °C, at 25 °C intervals. Parameters of interest include:

- liquid composition
- pressure: liquid vapour pressure, 10 MPa hydrogen (cold)
- iron sulphate catalyst/additive: not present, two concentrations (.1 and .5 wt%)

A matrix of up to 15 experiments, including three duplicates, is planned. (2 liquids X 2 pressures X 3 catalyst loadings + 3 duplicates)

Phase III: Liquid-Liquid Equilibria in the Product Materials

Liquid-liquid equilibria arising in product liquid samples supplied by CANMET will be evaluated over the temperature range 350 - 425 °C, at 25°C intervals. Parameters of interest include:

- liquid composition (low severity, high severity, high and low coal derived liquid concentrations)
- pressure: liquid vapour pressure, 10 MPa hydrogen (cold)
- iron sulphate catalyst/additive: not present, two concentrations (.1 and .5 wt%)

A minimum of 600 grams of each type of product liquid would be required (sufficient for 3 experiments), 1200 grams would be desirable. A total of 24 experiments are planned (4 liquids X 2 pressures X 3 catalyst concentrations).

Product liquids would preferrably be the unfractionated material exiting the reactor or recombined material closely approximating the composition of this stream (hydrogen will take the place of low molar mass species eg. methane, ethane, carbon dioxide etc. which are not readily recovered). Equilibria concerning product samples generated at U of T, from supplied materials, will be evaluated in addition to/ instead of product samples supplied by CANMET, if only limited quantities of product materials are available. These materials would be generated at appropriate reaction conditions approximating those employed at CANMET. Liquid samples can be generated in 700g batches. As all species with an appreciable mole fraction play a role in phase equilibria representative samples of stream contents area essential.

It would be worthwhile to evaluate a limited number of samples from the heavy oil only process, for comparative purposes. Such samples may well be readily available (an additional 4 experiments), eg. 2 liquid compositions X 1 pressure X 2 catalyst loadings)

Phase IV: Liquid-Liquid Equilibria in Mixtures of Feed and Product

The object of this phase is to determine whether phase splitting is sensitive to axial mixing patterns or coal concentration in coprocessing. Phase equilibria experiments will be performed as above with mixtures of product and feed materials (20, 50, and 80 wt% mixtures) and two mixtures of coal derived liquids and bitumen (50 wt% mixtures). 30 experiments are planned (5 liquid mixtures X 2 pressures X 3 catalyst loadings).